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Uranium-mediated activation of small molecules

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Polly L. Arnold*

[*]Corresponding author; e-mail: polly.arnold@ed.ac.uk

Chemical structures illustrating various coordination modes of ligands:

- $X_3U-O-C\equiv C-O-UX_3$
- X_3U and UX_3 coordinated to a $C=N=O$ ligand.
- X_3U and UX_3 coordinated to a $C\equiv N$ ligand.
- X_2U and UX_2 coordinated to a benzene ring.
- X_3U and UX_3 coordinated to a C_3O_2 ligand.

Molecular complexes of uranium are capable of activating a range of industrially and economically important small molecules such as CO, CO₂, and N₂; new and often unexpected reactions provide insight into an element that needs to be well-understood if future clean-energy solutions are to involve nuclear power.

The area of uranium-mediated small molecule activation chemistry has seen remarkable recent growth. The global drive towards low-carbon energy has renewed general interest in nuclear power and chemists have

important contributions to make in the behavioural understanding and design of new fuel materials, such as uranium nitrides and carbides, and custody and remediation of wastes from past, current, and future generation power plants.

Uranium and its compounds come into contact with elements from across the periodic table when fuel is mixed with additives, daughter products, and cladding materials, and during uranium mining and waste treatments; understanding its chemistry is a significant and important challenge. Small molecule reactions that reveal new structure and bonding motifs help with this, and unexpected results can provide theoreticians with new tests for their bonding models for these relativistic cations. This in turn allow them to better predict the properties of the unnatural, more radioactive and harder-to-handle actinides.

This highlight will focus on recent successes in the use of molecular uranium complexes to activate small molecules, which for this purpose may be defined as small, neutral, polyatomic molecules that are relatively (or very) thermodynamically stable or kinetically inert (or even both). These include important industrial feedstock chemicals such as CO, CO₂, and N₂. Progress has undoubtedly been facilitated by improvements in starting material syntheses, technologies such as paramagnetic NMR spectroscopic methods and single crystal X-ray diffraction, and in the analysis of large molecules by computational methods.

The behaviour of uranium in its complexes shows many sharp contrasts to the 4fⁿ lanthanides which have highly contracted f-orbitals, resulting in previous descriptions of its behaviour as that of a ‘big transition metal’; it sits formally in Group 6 below Cr, Mo, and W. The relative accessibility of its f-orbitals and electrons for bonding allow formal oxidation states between +2 and +6, although the +2 formal state has so far only been demonstrated in arene complexes in which the extra electron is reasonably described as residing in a ligand orbital (see below).

The reader seeking a more historical perspective is referred to the long and excellent reviews of uranium chemistry in chapters 5 and 25 of the new ‘bible’ of actinide and transactinide chemistry,¹ an interesting historical perspective on the sandwich molecule uranocene [U(η-C₈H₈)₂],² and a recent perspective on the future of homogeneous uranium catalysis.³ Those interested in learning more about the discovery of uranium and its original misidentification, and about how the growth of its molecular chemistry has been intertwined with the exploration of nuclear fuel and nuclear waste are guided to some short podcasts and commentary articles.⁴

2. Uranium(III)-mediated activations

Two reviews on the general reactivity of strongly reducing U(III) complexes appeared five years ago.⁵ The U^{III/IV} reduction couple is strongly affected by the ligands, and the high reactivity of U^{III} complexes combined with the propensity of the large metal to coordinate the donor solvents requisite for cyclic voltammetric

experiments demand caution in the design and interpretation of electrochemical studies. For example in THF solution, *vs.* ferrocene $[\text{Cp}_2\text{Fe}]^{1+/0}$, $[\text{Cp}_3\text{U}(\text{THF})]$ ($\text{Cp} = \text{C}_5\text{H}_5$) undergoes an irreversible oxidation at -1.01 V,⁶ $[(2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{O})_3\text{U}]$ displays a reversible oxidation at -1.22 V, and $[\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{U}]$ at -1.24 V,⁷ but the measured potentials probably correspond to THF solvates in each case. In a range of substituted cyclopentadienyl systems $[(\text{C}_5\text{H}_4\text{R})_3\text{UCl}]/[(\text{C}_5\text{H}_4\text{R})_3\text{UCl}]^-$ a very wide $\text{U}^{\text{IV/III}}$ oxidation potential range was measured, between -1.8 and -2.6 V *vs.* $[\text{Cp}_2\text{Fe}]^{1+/0}$.⁸ Interestingly in this case, the cyclopentadienyl electron richness did not correlate precisely with measured redox potential: cyclic voltammetric studies showed the U^{III} fragment increases in reducing power in the order $\text{R} = \text{SiMe}_3 < \text{H} < \text{CMe}_3 < \text{Me}$.⁹

Carbon oxides; CO

The bond in CO is the strongest in the periodic table, and an interesting target for activation being a key C1 feedstock in industry. Tris(trimethylsilylcyclopentadienyl) U^{III} was originally shown to bind CO reversibly in 1986.¹⁰ Following this, and up to 2003, more strongly bound CO adducts were reported, and single crystal structures were obtained for substituted analogues such as $[(\eta\text{-C}_5\text{Me}_4\text{H})_3\text{U}(\text{CO})]$.¹¹ with uranium–CO π -backbonding.¹² The complex $[(\text{Cp}^*)_3\text{U}]$ ($\text{Cp}^* = (\text{C}_5\text{Me}_5)$), originally considered too sterically encumbered to be isolable, has also been shown capable of reversible carbon monoxide binding; $[(\text{Cp}^*)_3\text{U}(\text{CO})]$, $\nu(\text{CO}) = 1922$ cm^{-1} . This contrasts with the lanthanide analogue $[(\text{Cp}^*)_3\text{Nd}]$ which forms a nonclassical carbonium ion complex, $[(\text{Cp}^*)_2\text{Nd}(\text{O}_2\text{C}_7\text{Me}_5)]$.¹³ The first non-organometallic uranium carbonyl complex was formed by reductive activation of a single CO molecule by two $\text{U}^{\text{III}}\text{L}$ complexes, in which L is a bulky hexadentate tris(aryloxide) N_3O_3 chelate $\{(\text{R}^i\text{ArO})_3\text{tacn}\}$ ($\text{R} = \text{Bu}^t$), and the CO is formally singly reduced upon binding as both a carbonyl and *iso*-carbonyl to the $[\{(\text{R}^i\text{ArO})_3\text{tacn}\}\text{U}^{3.5}]_2(\mu\text{-}\eta^1, \eta^1\text{-CO})$ **1**, Fig. 1, with a high $\nu(\text{CO}) = 2092$ cm^{-1} .¹⁴

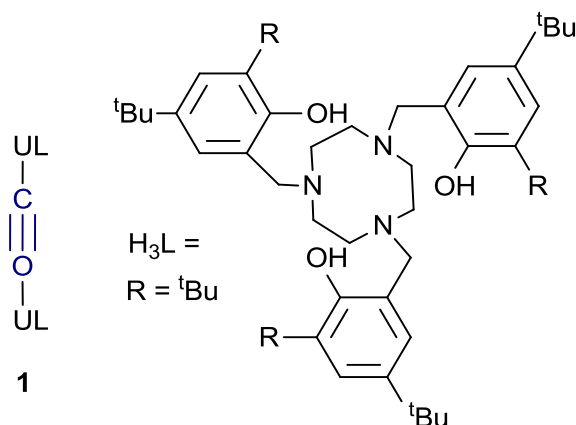


Figure 1. Drawing of the first non-organometallic uranium CO complex, which is both a carbonyl and an isocarbonyl complex.

Whilst many metal complexes are capable of catalysing the insertion of CO into other organic substrates, only a handful of complexes have demonstrated the C–C coupling of two metal-coordinated CO ligands since the direct dimerisation of CO to afford OCCO is energetically uphill by +73 kcal mol⁻¹. A breakthrough was provided by the sterically congested, trivalent, organometallic uranium complex [U(η-C₈H₆{Si^{*i*}Pr₃-1,4}₂)(Cp*)] which demonstrated unprecedented reductive trimerisation of CO to the triangular, cyclic C₃O₃ dianion **3**, Fig. 2, or deltate dianion, bridging two U^{IV} centres.¹⁵ The same U^{III} complex is also capable of reductively coupling CO to [C₂O₂]²⁻ if 0.95 equivalents of CO gas is used, although no interconversion between the (CO)_{*n*} homologues, or subsequent reactivity, has been demonstrated to date.¹⁶ The series of dianions of reduced CO are a set of cyclic aromatic oxocarbons whose pleasingly simple [C_{*n*}O_{*n*}]²⁻ generic structure belies their challenging and individual syntheses. Subtle manipulation of the steric environment of the complex allowed the cyclic C₄O₄, or squarate, dianion to be formed by CO reduction at [(U(η-C₈H₆{Si^{*i*}Pr₃-1,4}₂)(η-C₅Me₄H)], **4**, Fig. 2.¹⁷

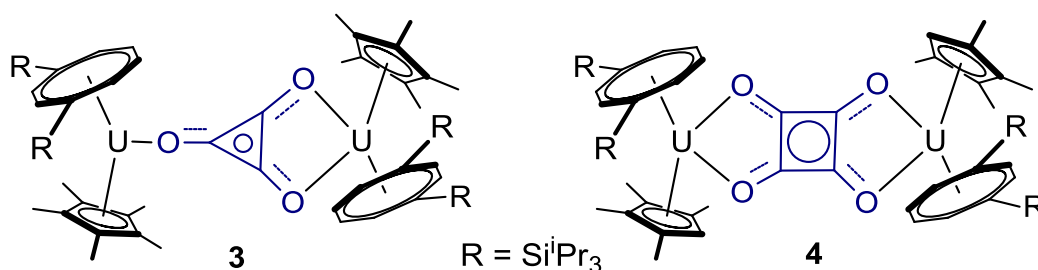


Figure 2. Complexes formed from the oligomerisation of CO.

The tris(amido) complex of uranium(III) UN''₃, where N'' is the hydrocarbon-soluble, sterically demanding, bis(alkylsilyl)amido monoanion [N(SiMe₃)₂]⁻, is widely used as a reagent in coordination chemistry, and it has generally been regarded not to possess any interesting small molecule activation chemistry of its own, despite its pyramidal structure. The 1979 report of its synthesis reported the authors' surprise at the absence of reactivity with CO or similar Lewis bases.¹⁸ Recently, we found that in alkane or arene solvents, or even in diethyl ether, UN''₃ does in fact react at ambient temperatures and pressures with carbon monoxide to afford a reductively coupled ynediolate [OCCO]²⁻ unit in **5**, Fig. 3.¹⁹ The ynediolate product forms exclusively, an observation we ascribe to the steric congestion around the OCCO unit, and although we were able to demonstrate further reactivity of this coupled unit for the first time, it was only in an intramolecular sense, cleanly forming new C–H and C–C bonds by the formal addition of one silylmethyl C–H across the alkyne bond in **6**, which contains the dianionic [OC(H)C(R)O]²⁻ fragment, as the sole product.

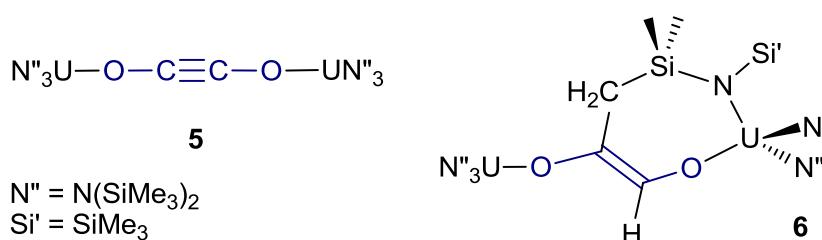


Figure 3. Complexes formed from the dimerisation of CO, and the product of C–C and C–H bond formation.

Perhaps of even greater surprise is that the simple tris(aryloxide) complexes $[\text{U}(\text{OAr})_3]$ ($\text{OAr} = \text{OC}_6\text{H}_3\text{-Bu}^t\text{-2,6,}^{20}\text{OC}_6\text{H}_2\text{-Bu}^t\text{-2,4,6}$) are also capable of exclusively coupling excess atmospheric CO to form $[\text{U}(\text{OAr})_3]_2(\mu\text{:}\eta^1, \eta^1\text{-C}_2\text{O}_2)$.²¹ This may well turn out to be a result of general applicability to bulky, oxophilic, reducing metal complexes that have a single electron reduction potential of -1.2 V or stronger (see above).

Carbon oxides; CO₂

Meyer's sterically encumbered ligand system also allows the isolation of an unusual linear, O-bound CO₂ molecule, $[\{(\text{AdArO})_3\text{tacn}\}\text{U}(\eta^1\text{-OCO})]$ ($\text{Ad} = \text{adamantyl}$), **7**, in Fig. 4, in which the CO₂ stretch in the IR spectrum at 2188 cm^{-1} suggests a small degree of activation of the CO₂, but the X-ray bond distances suggest a greater degree activation.²² The bonding in the UOCO fragment is still a subject of debate, since different resonance structures may be drawn for the linearly coordinated ligand, but the pale colour of the CO₂-bound product suggests a formal U^{IV} oxidation state.²³ The use of the smaller ligand ($\text{R} = \text{Bu}^t$) resulted in CO₂ reduction to CO and O, both fragments of which are trapped by U^{III} and characterised.²³ This compares neatly with the 1991 report of the isolation of $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}]_2(\mu\text{-O})$ from the reaction of CO₂ or N₂O with $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}]$.²⁴ The strong M–O bonds and U^{IV} oxidation state means that U^{IV}-O-U^{IV} is a common motif in uranium small molecule chemistry; in this case it is not clear whether the authors looked for an associated isocarbonyl U(CO)U product in the products. Insertion of CO₂ into a U–O bond in $\text{U}(\text{OC}_6\text{H}_2\text{-Bu}^t\text{-2,4,6})_3$ proceeds as anticipated to form the arylcarbonate but an additional CO₂ reduction to a $\mu\text{-O}$ fragment was also observed, affording $[\text{U}_2(\text{OAr})_4(\mu\text{-O})(\mu\text{:}\eta^1, \eta^1\text{-O}_2\text{COAr})_3]_2$.²¹

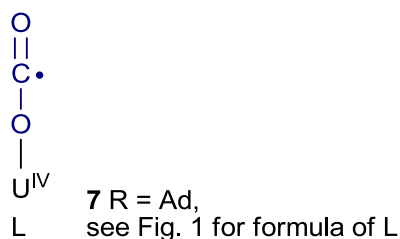


Figure 4. One resonance isomer for the linear CO₂ complex formed at a sterically encumbered complex.

Nitrogen oxides; NO

To date no uranium nitrosyl complexes have been reported, despite the clear similarity between CO and NO as π -acid ligands. The most common reaction observed for U^{III} complexes has always been NO and N_2O deoxygenation to form U^{IV} -O- U^{IV} complexes (see also above). It was recently commented that $[U(\eta-C_8H_6\{Si^iPr_3-1,4\}_2)(Cp^*)]$ did not bind NO as a simple π -acid, which seems reasonable as the molecule was so strongly reducing towards CO. Interestingly, a 2 : 1 mixture of CO and NO was cleanly transformed into the product of NO deoxygenation *and* CO coupling, *i.e.* a U^{IV} cyanate $[U(\eta-C_8H_6\{Si^iPr_3-1,4\}_2)(Cp^*)(\mu-NCO)]_2$, **8** in Fig. 5, and an equimolar amount of the U^{IV} -O- U^{IV} complex as byproduct.²⁵ The disorder in the X-ray structure between the O and N positions in the bridges preclude meaningful detailed analysis, but confirm again that the weaker of the two (NO rather than CO) diatom bonds have been cleaved.

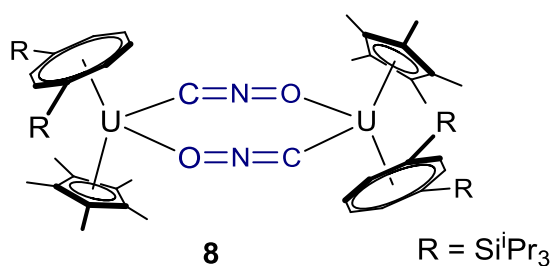


Figure 5. A complex formed from the combined activation of CO and NO.

Dinitrogen

The Haber-Bosch process that converts N_2 to ammonia consumes approximately 2% of the world's energy production, so mild routes to N_2 activation and functionalisation are of continuing interest. The first Haber-Bosch reaction vessels used heterogeneous osmium and uranium catalysts, and uranium nitrides are candidate future nuclear fuels. As a π -acid, molecular N_2 was first shown to coordinate to a reducing U^{III} centre by Scott in 1998, forming the weakly-bound side-on N_2 tren complex $[\{ N(NCH_2CH_2NSiBu^tMe_2)_3U \}_2 (\mu:\eta^2, \eta^2-N_2)]$ ²⁶ and by Cummins forming the more reduced end-on N_2 $[\{ C_6H_3Me_2-3,5 \}_2 (Bu^tN)_3 U (\mu:\eta^1, \eta^1-N_2)] Mo \{ N(Bu^t)Ph \}_3$.²⁷ Since then, remarkably few examples have been isolated, in contrast with the hundreds of d-block N_2 complexes that are now known, and which are beginning to show some remarkable functionalisation chemistry. Despite the formal reduction to (N_2^{2-}) , 80 psi of N_2 are required to stabilise $[(Cp^*)_3U(\eta^1-N_2)]$,²⁸ which, like the CO complex, shows virtually no change in the UCp^*_3 fragment geometry on binding the diatom. Lower (5 psi) overpressures are required to keep the N_2 bound, despite its formal reduction, in $[(Cp^*)(\eta-C_8H_6\{Si^iPr_3-1,4\}_2)U]_2(\mu-N_2)$, **9** in Fig. 6.²⁹ Again, of surprise to us was the finding that

$[\text{U}(\text{OAr})_3]$ can both bind N_2 in a side-on manner to form $[\text{U}(\text{OAr})_3]_2(\mu\text{:}\eta^2, \eta^2\text{-N}_2)$, similarly to **9**, although the significantly increased thermal stability of the *tri*- compared to the *di-t*-Bu analogue is still not clear.²¹

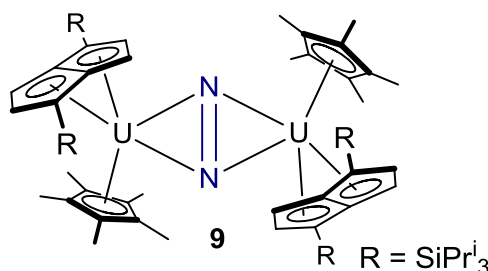


Figure 6. A complex formed from the reductive activation of N_2 .

Reduction of the polypyrrolide complex $[\text{K}(\text{dme})][(\text{Et}_8\text{-calix}[4]\text{tetrapyrrole})\text{U}(\text{dme})]$ under an N_2 atmosphere afforded a remarkable complex arising from reductive cleavage of N_2 in a reaction in which N_2 , solvent DME, and siloxane grease molecules are all reductively cleaved.³⁰ Crystallographic characterisation formulated the product as $\text{U}^{\text{V}}/\text{U}^{\text{IV}} [\text{K}(\text{dme})_4][\{\text{K}(\text{dme})\}_2[(\text{Et}_8\text{-calix}[4]\text{tetrapyrrole})\text{U}\}_2(\mu\text{-NK})_2]$, but the material is always associated with a small amount of a μ -oxo product, evidencing the high reactivity of this system, and the difficulty of working with these strongly reducing complexes. Sadly, no further reactivity of this complex has been reported.

Alkane C–H bonds

Perhaps surprisingly, there have been no reports of the cleavage of unactivated hydrocarbon C–H bonds by uranium complexes. However, the molecular structures of some solvated adducts of Meyer's U^{III} ($^t\text{BuArO})_3\text{tacn}^{3-}$ complex suggested the presence of an alkane coordinated in the pocket, $\text{U}(\text{L})\text{R}_3$ ($\text{L} = (^t\text{BuArO})_3\text{tacn}$, $\text{R} = \text{methylcyclo-hexane}$), **10** in Fig. 7.³¹ The suggested coordination mode was supported by a computational analysis. Only a handful of examples of this type of metal-CH interaction have been characterised in either the solution or solid state prior to this.

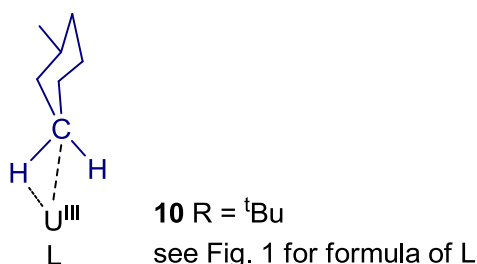


Figure 7. An alkane adduct suggested by X-ray crystallography and DFT calculations.

Arenes and alkynes

Two U^{III} cations can bind and partially reduce arenes such as benzene and toluene to make complexes that formally are synthons for U^{II} , an otherwise inaccessible oxidation state for uranium. The complexes $[\{C_6H_3Me_{2-3,5}\}_2(Ad)N\}_2U](\mu:\eta^6,\eta^6\text{-arene})$ (arene = benzene, toluene, **11** in Fig. 8),³² $K_2[(Mes[{}^iBu]CN)_3U]_2(\mu:\eta^6,\eta^6\text{-}C_{10}H_8)$,³³ and $[(Cp^*)_2U]_2(\mu:\eta^6,\eta^6\text{-}C_6H_6)$ ²⁸ show no further reactivity involving the arene, but rather reduction chemistry *via* arene displacement. For example, the activation and coupling of alkynes, which displace the arene, forming the $\mu:\eta^4,\eta^4\text{-}C_4Ph_4$ cyclic dianion coordinated by the two uranium cations.³⁴ As an aside, a divalent thorium synthon has also been prepared, **12** in Fig. 8, and shows interesting azide and CO_2 chemistry.³⁵

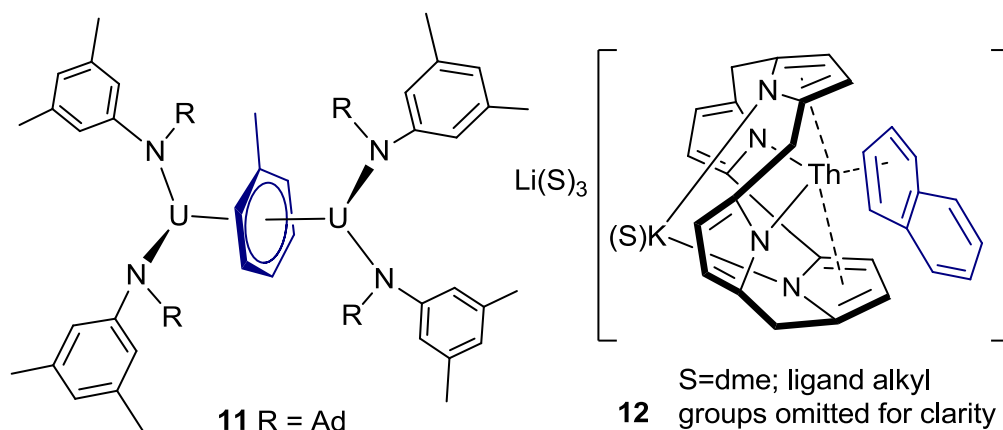


Figure 8. Complexes formed from the reduction of arenes.

2. Uranium(IV)-mediated activations

Uranium in its higher oxidation states shows a different range of reactivities, although reductive activation is still possible. The formal states U^{IV} and U^{VI} are most commonly found, but many stable examples of complexes exist for U^{IV} , U^V , and U^{VI} . A few selected examples are described below.

Alkane C–H bonds

Following the seminal work on methane activation by $[(Cp^*)_2LnMe]$ ³⁶ complexes in the 1980s it was shown that Th^{IV} alkyl complexes $[Cp^*_2Th(CH_2)_2C(CH_3)_2]$ ³⁷ also activated methane and alkane C–H bonds *via* σ -bond

metathesis chemistry. However, no further chemistry with U^{IV} and simple alkanes has been reported since. Instead many examples of C–H metallation chemistry have been shown by organouranium complexes, both with sp^2 and sp^3 C–H bonds. All take place within the coordination sphere of the metal, either as part of ligand metallation steps, or after precoordination of the substrate through a heteroatom such as N or O, even Te.³⁸

A recent computational study on methane C–H bond activation by gas phase Th^+ and U^+ ions is of interest;³⁹ the metal cations exhibit different reactivity on account of different electronic configurations of the bare cations and Th^+ is the only actinide that activates exothermically the methane C–H bond.

Alkynes

The first alkyne π -complex was isolated and crystallographically characterised at the start of the decade: $[(Et_2N)_2U(C\equiv C'Bu)(\eta^2-HC\equiv C'Bu)][BPh_4]$ was also shown to be shown to be an active catalytic precursor for the selective dimerization of terminal alkynes.⁴⁰ Since then, a variety of organo- U^{IV} complexes such as $[(Cp)_2UMe_2]$ have been demonstrated to be convenient precatalysts for the oligomerization of terminal alkynes, and the coupling of terminal alkynes and isonitriles ($RN\equiv C$), generating (E)-alkynylimines by 1,1-insertion of an isonitrile into the uranium–acetylide bond.⁴¹

The rather unusual terminal oxo complex $[(Cp^f)_2U=O]$ ($Cp^f = C_5H_2Bu'_3-1,2,4$) does not exhibit cycloaddition behaviour with alkynes, suggesting that the double bond is best described as polar with a major resonance structure $[U^+-O^-]$. It does react as a nucleophile with Me_3SiCl to give $[(Cp^f)_2U(OSiMe_3)Cl]$, confirming this bonding description.⁴² The monomeric imido complex $[(Cp^f)_2U = NMe]$ reacts with alkynes to form the cycloaddition products.⁴³

Carbon oxides; CO and CO₂

The insertion (rather than reduction) of CO and CO₂ into trivalent organolanthanide and tetravalent organoactinide $Ln-C$ and $Ln-H$ σ -bonds has been known since the 1980s, and leads to the formation of acyl ligands and bidentate carboxylate ligands respectively. Progress in CO insertion chemistry has recently been made by Evans, Berthet, and Ephritikhine.

The double ‘tuck-in’ complex $[(\eta^5:\eta^1-C_5Me_4SiMe_2CH_2)_2U]$ readily inserts CO or CO₂ into both U–C σ -bonds to form $[(\eta^5:\eta^1-C_5Me_4SiMe_2\{=CH_2\}CO)_2U]$, **13** in Fig. 9,⁴⁴ and $[(\eta^5:\eta^1-C_5Me_4SiMe_2CH_2CO_2)_2U]$, **14** in Fig. 9,⁴⁵ respectively. Likewise $[(Cp^*)_2U(CCCPh)_2]$ inserts CO₂ cleanly to give $[(Cp^*)_2U(O_2CCCPh)_2]$.⁴⁶

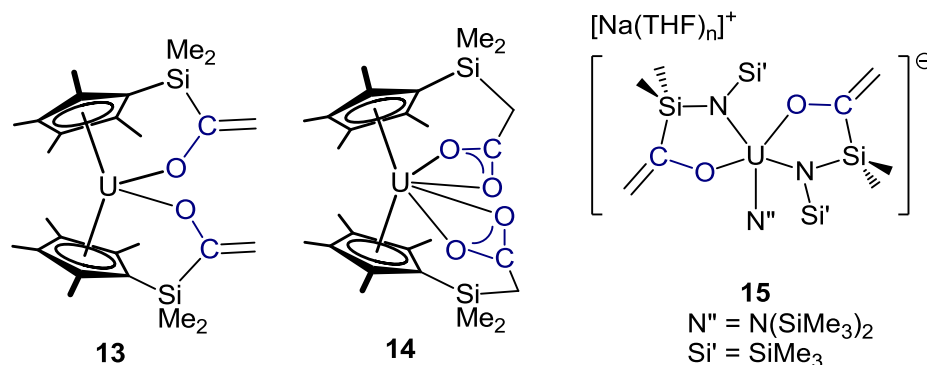


Figure 9. Complexes formed from the insertion of CO and of CO₂.

The complex $[\text{Na}(\text{THF})\text{UN}''(\text{CH}_2\text{SiMe}_2\text{N}\{\text{SiMe}_3\})_2]_n$ ($N'' = \text{N}(\text{SiMe}_3)_2$) contains two metallated silylmethyl groups, which both react to insert CO into the U–C bond to form $[\text{Na}(\text{THF})\text{UN}''(\text{OC}\{\text{CH}_2\}\text{SiMe}_2\text{N}\{\text{SiMe}_3\})_2]$, **15** in Fig. 9,⁴⁷ analogously to Dormond's previous observation of CO insertion into the monomethyl U^{IV} analogue $[\text{MeUN}''_3]$,⁴⁸ with the U–N bond unaffected. In this case the reaction is rapid at ambient pressure, a fact attributable to the strongly nucleophilic character of the CH₂ group in this molecule. The same complex also inserts CO₂ in the manner that would be predicted, forming $[\text{Na}(\text{THF})(\text{NC}_5\text{H}_5)_2\text{UN}''(\text{OC}\{\text{O}\}\text{CH}_2\text{SiMe}_2\text{N}\{\text{SiMe}_3\})_2]$.

3. Uranium(V) and Uranium(VI)-mediated activations

The most prevalent small molecule reactions reported to date involve the conversion of the U=NR imido double bond in a complex to the stronger U=O double bond, *e.g.* the terminal oxo complex $[\{(\text{R}^{\text{ArO}})_3\text{tacn}\}\text{U}=\text{O}]$ is formed when the U^V imido precursor is treated with CO₂, probably *via* a cycloaddition reaction, releasing a molecule of isocyanate. The U^V oxo is very short and highly polarised.⁴⁹ The same imido complex $[\{(\text{R}^{\text{ArO}})_3\text{tacn}\}\text{U}=\text{NSiMe}_3]$ ($\text{R} = \text{Ad}$) reacts with CO to form the isocyanate $[\{(\text{Ad}^{\text{ArO}})_3\text{tacn}\}\text{U}(\eta^1\text{-NCO})]$.⁵⁰ Another notable exception to U=O formation is that the remarkable bis(imido) uranyl analogue $[\text{U}(=\text{NBu}^t)_2\text{I}_2\text{S}_2]$ ($\text{S} = \text{OPPh}_3$),⁵¹ does not form the oxo-imido complex $[\text{U}(=\text{NBu}^t)(=\text{O})\text{I}_2\text{S}_2]$ from treatment with $\text{PhN}=\text{C}=\text{O}$, instead imido transfer takes place forming $[\text{U}(=\text{NBu}^t)(=\text{NPh})\text{I}_2\text{S}_2]$. This surprising result is explained in that the formation of the intermediate in the [2 + 2] cycloaddition of the isocyanate C=N bond across the U=N imido is more important in defining the reaction path than the overall thermodynamic preference for the U=O bond formation.⁵² The reactions of Lewis-acid-activated U^{VI} oxocomplexes with aminosilanes and weak CH-bond containing hydrocarbons have afforded pentavalent uranyl complexes with silylated and functionalised oxo groups,⁵³ whilst uranyl iodide $[\text{UO}_2\text{I}_2]$ (but not the more stable chloride) reacts with Me_3SiX ,⁵⁴ and $[\text{UO}_2(\text{ArNC}(\text{Ph})\text{CHC}(\text{Ph})\text{O})_2]$ ($\text{Ar} = 3,5\text{-Bu}^t_2\text{C}_6\text{H}_3$) reacts with Me_3SiI (but not the more

stable chloride)⁵⁵ to form U^{IV} products resulting from oxo silylation. Whilst not exactly ‘inert small molecules’ these few reactions suggest there is much potential for further reactivity of $U=O$, $U=N$, and perhaps also the transiently stable $U\equiv N$ ⁵⁶ bond still to be explored.

4. Conclusions and outlook

A large and fascinating array of small molecule activation chemistry by uranium complexes has been uncovered in the last decade, primarily based on reductive activation using molecular U^{III} complexes, and often facilitated by the thermodynamic bond strength of the $U-O$ bond. Opportunities still remain for the further functionalisation of these small molecules, and for their inclusion in homogeneous catalytic cycles. For this to be achieved, molecules will need to be designed such that the reduction of the U^{IV} adducts allows for product removal, without the loss of other ligands from these metals. This will not be a simple task for f-block complexes which display facile ligand redistribution chemistry.

In some cases U^{III} molecules have proven too reactive; for example only products arising from O atom abstraction are found in many reactions with CO_2 and nitrogen oxides. Evans recently showed that reductive molecular lanthanide chemistry allows the isolation of the first f-block NO complex; NO is coordinated as a dianion in $[\{N''_2(THF)Y\}_2(\mu:\eta^2, \eta^2-NO)]$ formed from exposure of the $(N_2)^{3-}$ complex $K[N''_2(THF)Y]_2(\mu:\eta^2, \eta^2-N_2)$ to 1.5 equivalents of NO gas.⁵⁷ Calculations on the NO complex show that a metal $d\pi$ to ligand π^* interaction is crucial for stability, suggesting that the appropriate low-oxidation state uranium complex should be able to coordinate NO as a ligand.

The stabilisation of low oxidation state uranium arene complexes noted above makes the absence of a U^0 bis(arene) sandwich more notable. Cloke has used metal vapour synthesis (MVS) to make zerovalent arene and heteroarene complexes of most of the lanthanides, using bulky tri-*tert*-butyl substitution to stabilise the strongly coloured, zero oxidation state complexes $[Ln(\eta^6-C_5E-Bu'_3-2,4,6)_2]$ ($E = C, N, P$).⁵⁸ Despite methods that overcome the difficulties of generating uranium vapour, no uranium(0) sandwich complex has yet been isolated from MVS or any solution reaction study.

Following the remarkable hydrocarbon C–H bond activation shown by the non-redox active organometallic Ln^{III} and Th^{IV} complexes described above, there must be opportunities for the higher oxidation state uranium complexes with appropriate ligand sets to participate in similar σ -bond metathesis chemistries.

Although very few reactions of $U^{V/VI}$ complexes with diatomic and triatomic small molecules have been reported this is bound to change soon as more anaerobic chemistry of hexa- and pentavalent uranyl and its imido analogues is uncovered.⁵⁹

The fact that a uranium cation has access to more bonding orbitals than a transition metal cation, a wide number of oxidation states, and the capacity to form many multiple bonds at the same time, suggests that with careful control the right complexes should exhibit reactions with small molecules not possible for any metal above it in the periodic table.⁶⁰

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